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# The Metal-to-Ligand Charge-Transfer Luminescences of Ruthenium(II)–Polypyridine–Tetraam(m)ine Complexes. Support for the Interconvertibility of Optical and Thermal (Kinetic) Franck–Condon Parameters

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This is the first report of the metal-to-ligand charge-transfer (MLCT) emission spectra of the bis-ethylenediamine– and tetraammine–bipyridineruthenium(II) complexes. The emission maxima occur at 800 and 840 nm, respectively, at 77 K in DMSO/$H_2O$ glasses. The MLCT excited states of these complexes have short lifetimes (less than 50 ns), and as a consequence, the emission intensities are very small. The energies of the emission maxima are very close to those expected on the basis of the difference in reduction potentials of the metal and ligand ($\Delta E_{1/2}$) and the values of the reorganizational free energies ($\chi_r$) of the vertical transitions estimated from the electron-transfer self-exchange reactions of the complexes ($h\nu_{max}(em) \cong F\Delta E_{1/2} - \chi_r$, where $F$ is Faraday's constant). The low energy of the emissions is in large part a consequence of the substantial contributions of the reorganizational free energies.

We have found that the metal-to-ligand charge-transfer (MLCT) luminescences of several mixed ligand, am(m)ine–polypyridine, complexes of ruthenium(II) (in 77 K glasses) appear in the midrange near-infrared (NIR) region, Figure 1. It has been alleged[1] that the $[Ru(NH_3)_4(bpy)]^{2+}$ complex does not emit. Furthermore, the emission properties of $[Ru(en)_2(bpy)]^{2+}$ described in the same report[1] are not significantly different from those of the bis-bipyridine complex. The earlier report was in accord with the general expectation that the MLCT excited states of many of these am(m)ine complexes would be efficiently quenched by a lower energy ligand-field (LF) excited state of the ruthenium(II) center.[1,2] The basis for this expectation is not altogether obvious since it depends on the relative ordering of the energies of the LF and MLCT excited states at their potential energy (PE) minima. The energies of the respective absorption maxima are not simply related to the energies of the PE minima since the energies of both kinds of transition contain reorganizational contributions that arise from the differences in geometry, solvation, etc. of the ground and excited electronic states; for $E_{ge}{}^{00}$ the energy of excited-state PE minimum, and $\lambda_r$, the net reorganizational energy contribution[3]

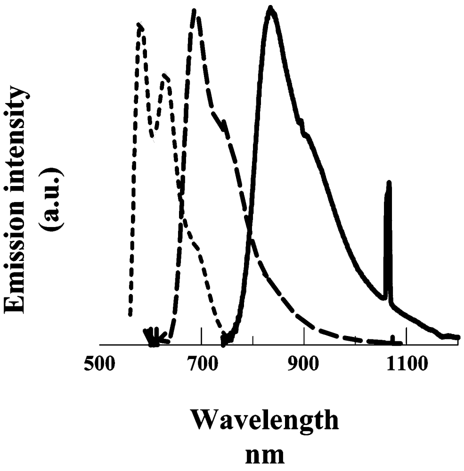

**Figure 1.** Emission spectra in DMSO–water glasses at 77 K of $[Ru(bpy)_3]^{2+}$ (left), $[Ru(NH_3)_2(bpy)_2]^{2+}$ (middle), and $[Ru(NH_3)_4(bpy)]^{2+}$ (right). The spectra were obtained separately and then superimposed; the intensity scales are arbitrary and different for each complex. The sharp line at 1064 nm is second-order scattered light from the laser used for excitation.

$$h\nu_{max}(abs) = E_{ge}{}^{00} + \lambda_r \tag{1}$$

While there is no doubt that the LF excited states of am(m)ine complexes are appreciably lower in energy than those of their polypyridine analogues,[4-6] the energies of the MLCT excited states are also expected to decrease when bipyridine is replaced by am(m)ines.[4,7-13] The energy contributions can be treated relatively simply for the MLCT absorption

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(1) Kobayashi, H.; Kaizu, Y. *Coord. Chem. Rev.* **1985**, *64*, 53.

(2) Ford, P. C. In *Inorganic and Organometallic Photochemistry*; Wrighton, M. S., Ed.; American Chemical Society: Washington, D.C., 1978; Vol. 168, p 73.

(3) In this paper $\lambda_r$ and $\chi_r$ refer to the reorganizational energy and reorganizational free energy contributions that correlate with low-frequency vibrational modes of the system.

(4) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.

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**Table 1.** Relationships between Optical and Thermal Properties of $[Ru(Am)_{6-2n}(bpy)_n]^{2+}$ Complexes[a]

| complex | $h\nu_{max}$ (abs) (ambient)[b] | $h\nu_{max}$ (em) (77 K)[c] | $F\Delta E_{1/2}$[d] | $\chi_r^\circ$ $(RuL^{3+,2+})/2$[e] | ~300 K shift expected[f] | 77 K shift obsd |
|---|---|---|---|---|---|---|
| $[Ru(bpy)_3]^{2+}$ | 21.8 | 17.2 | 21.1 | 3.4 | 0 | 0 |
| $[Ru(en)(bpy)_2]^{2+}$ | 20.16 | 16.0 | 19.2 | 3.9 | 2.4 | 1.2 |
| $[Ru(NH_3)_2(bpy)_2]^{2+}$ | 20.4 | 14.3 | 18.8 | 4.0 | 2.9 | 2.9 |
| $[Ru(en)_2(bpy)]^{2+}$ | 19.0 | 12.5 | 18.1 | 5.2 | 4.8 | 4.7 |
| $[Ru(NH_3)_4(bpy)]^{2+}$ | 19.1 | 11.9 | 17.7 | 5.4 | 5.4 | 5.3 |

[a] All energies in units of ($10^{-3} \times$ cm$^{-1}$ = $\mu$m$^{-1}$). Spectroscopic band maxima are from the raw, not deconvoluted, spectra. [b] In ambient DMSO/$H_2O$ (1/1) solutions.[8] [c] In DMSO/$H_2O$ (1/1) glasses at 77 K. [d] $\Delta E_{1/2} = [E_{1/2}(Ru^{III}/Ru^{II}) - E_{1/2}(bpy/bpy^-)]$; electrochemical measurements in ambient acetonitrile with tetrabutylammonium hexafluorophosphate electrolyte. [e] Reorganizational free energies based on experimental rate constants for self-exchange electron-transfer reactions, $\chi_r^\circ \cong RT\ln(k_{et}/K_A\kappa_{el}\nu_{nu})$.[8-10,19] This corresponds to a limit in which there is no electronic delocalization between the donor and acceptor, generally, $\chi_r < \chi_r^\circ$. [f] The difference between data in columns 4 and 5 for $[Ru(bpy)_3]^{2+}$ and the other complexes, $\Delta h\nu_{max}$(em; expected) = $([F\Delta E_{1/2} - \chi_r]_{ref} - [F\Delta E_{1/2} - \chi_r]_{complex})$, assuming that $\chi_r = [\chi_r(RuL^{3+,2+}) + \chi_r(bpy/bpy^-)]/2$, where $RuL^{2+}$ is the complex indicated ion column 1; $\chi_r(bpy/bpy^-)$ is treated as a constant in this comparison.

maxima. Since energies and free energies are equivalent for vertical transitions (provided all terms are consistent, as discussed elsewhere),[9,14,15] and the free energy quantities are related to the readily measured differences in metal and ligand reduction potentials (for $E_{ge}^{00}$),[7-9,12,13,16] the reorganizational free energy, $\chi_r$,[3] can be based on the kinetics of self-exchange electron-transfer reactions.[8,9,12,13,15-19] Then, a useful approximate relationship is[8]

$$h\nu_{max}(abs) = F\Delta E_{1/2} + \chi_r \tag{2}$$

It is important to note that the reorganizational free energy of the $[Ru(NH_3)_6]^{3+,2+}$ couple is about twice as large as that of $[Ru(bpy)_3]^{3+,2+}$.[10,19,20] Since the $Ru^{III}/Ru^{II}$ reduction potentials decrease more markedly than the $bpy/bpy^-$ reduction potentials when bipyridine (bpy) is replaced by an am(m)ine,[10,19,20] this tends to decrease the MLCT transition energy. Thus, the variations in $F\Delta E_{1/2}$ and $\chi_r$ are expected to somewhat compensate in the MLCT absorption spectra, so these vertical transitions are not of themselves representative of the variations in $E_{ge}^{00}$ (see Table 1).

Large reorganizational free energy contributions are expected to result in relatively low energy emission spectra; neglecting the singlet−triplet energy difference (twice the exchange energy):[8,9,11,13,21]

$$h\nu_{max}(em) \cong F\Delta E_{1/2} - \chi_r \tag{3}$$

This suggests that the tetraam(m)ine−polypyridine $Ru^{II}$ MLCT emission spectra should occur at relatively low energies (Table 1). These estimates of $(E_{ge}^{00} - \lambda_r)$[9,10,13,19] have led us to search for such spectra. Initial studies with a Si-based diode array were encouraging,[22] but we have only been able to resolve reliable spectra with a Princeton Instruments OMAV/InGaAs array detector and an Acton SP500 spectrometer (wavelength calibration with respect to Xe emission lines and intensity calibration relative to the output of a NIST-traceable quartz−tungsten−halogen lamp). The emissions of the tetraam(m)ine complexes are very weak, and we have found them to be obscured by scattered light in commercial fluorimeters. The scattered light problems are minimized and readily identified when laser excitations are used (Figure 1); the emission spectra of these complexes obtained using 473 and 532 nm excitations from cw solid-state lasers were indistinguishable. The energies of the 77 K MLCT emission maxima of the series of complexes, $[Ru(Am)_{6-2n}(bpy)_n]^{2+}$ (Am = $NH_3$ or en/2; $n$ = 1, 2, or 3), are consistent with the variations of their differences in metal and ligand reduction potentials, Figure 2. The correlation in Figure 2 is qualitatively in accord with expectation for the MLCT emission spectra of a series of related complexes. However, it is emphasized that the conditions for the spectral and electrochemical measurements are very different (77 K glasses and ambient solutions, respectively), and that the reorganizational free energies (and probably the exchange energies)[11,21] vary systematically in the same order as $F\Delta E_{1/2}$ (Table 1).

The importance of the comparisons in Figure 2 and Table 1 is that they are simple, and they provide an easy means of estimating the energy range of an expected MLCT emission. Rigorous correlations, involving measurements in the same media (see comments above and in Table 1) and deconvolution of the spectra to evaluate the energies, relative intensities, and bandwidths of the 0−0′ and vibronic

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(5) Lever, A. B. P.; Solomon, E. I. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; Wiley: New York, 1999; Vol. I, p 1.

(6) Figgis, B. N.; Hitchman, M. A. *Ligand Field Theory and its Applications*; Wiley-VCH: New York, 2000.

(7) Lever, A. B. P.; Dodsworth, E. In *Electronic Structure and Spectroscopy of Inorganic Compounds, Vol. II*; Lever, A. B. P., Solomon, E. I., Eds.; Wiley: New York, 1999; p 227.

(8) Gorelsky, S. I.; Kotov, V. Y.; Lever, A. B. P. *Inorg. Chem.* **1998**, *37*, 4584.

(9) Seneviratne, D. S.; Uddin, M. J.; Swayambunathan, V.; Schlegel, H. B.; Endicott, J. F. *Inorg. Chem.* **2002**, *41*, 1502.

(10) Endicott, J. F. In *Electron Transfer in Chemistry. Vol. 1*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 1, p 238.

(11) Endicott, J. F.; Schegel, H. B.; Uddin, M. J.; Senerivatne, D. *Coord. Chem. Rev.* **2002**, *229*, 95−106.

(12) Endicott, J. F.; Uddin, M. J. *Coord. Chem. Rev.* **2001**, *219−221*, 687.

(13) Endicott, J. F.; Uddin, M. J.; Schlegel, H. B. *Res. Chem. Intermed.* **2002**, *28*, 761.

(14) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

(15) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078.

(16) Graff, D.; Claude, J. P.; Meyer, T. J. In *Electron Transfer in Organometallic and Biochemistry*; Isied, S. S., Ed.; American Chemical Society: Washington, D.C., 1997; p 183.

(17) Gould, I. R.; Noukakis, D.; Luis, G.-J.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

(18) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4963.

(19) Endicott, J. F. In *Comprehensive Coordination Chemistry II, Vol. 7, From the Molecular to the Nanoscale: Properties*; Creutz, C., Vol. Ed.; McCleverty, J., Meyer, T. J., Eds.; Pergamon: Oxford, U.K.; Chapter 7.1, pp 1−78.

(20) Meyer, T. J.; Taube, H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987.

(21) Lever, A. B. P.; Gorelsky, S. I. *Coord. Chem. Rev.* **2000**, *208*, 153.

(22) Seneviratne, D., Ph.D. Dissertation, Wayne State University, Detroit, MI, 1999.

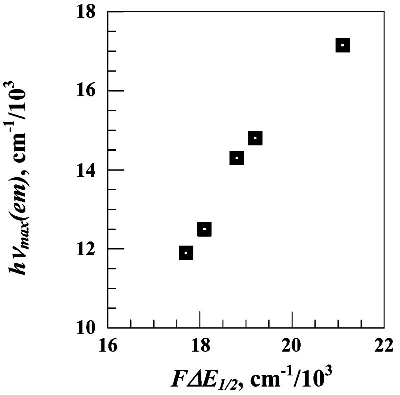

**Figure 2.** Correlation of 77 K emission maxima for $[Ru(Am)_{6-2n}(bpy)_n]^{2+}$ complexes with the difference in $Ru^{III}/Ru^{II}$ and bpy/bpy$^-$ reduction potentials (the complexes in the figure are ordered, top to bottom, as in Table 1).

components can provide important additional information; they may permit evaluation of exchange energy contributions[9,13,21] and the effects of anharmonicities that arise from configurational mixing.[9,11,13,23,24] An important effect of the configurational mixing between the ground and excited electronic states in these complexes is the progressive attenuation reorganizational energy contributions as the emission energy decreases;[9,23,24] this effect is most evident in the systematic decrease in the intensity of the vibronic sidebands of the spectra in Figure 1. These points will be addressed in detail in a later report. From a conceptual point of view, it is important to observe that these details, while important, amount to fine structure and the larger features of MLCT spectroscopy can be treated in terms of simple electron-transfer concepts.[10−13]

The difficulties encountered in previous attempts to detect tetraam(m)ine−polypyridine−ruthenium(II) emission spectra undoubtedly have arisen from the difficulty in detecting emissions at these relatively long wavelengths and from the small emission intensities. The shift of $h\nu_{max}$(em) values to low energies is consistent with the relatively large reorganizational free energy contributions. Although one expects solvent reorganizational energy contributions to be attenuated in the glassy medium, bandwidths of the fundamental components of the deconvoluted emission spectra do increase with the number of am(m)ines through the series of complexes. The small intensities of these emissions correlate with their very short lifetimes; our preliminary results indicate that the 77 K lifetime of the MLCT emission of $[Ru(NH_3)_4(bpy)]^{2+}$ is ca. 25 ns. Thermally activated crossing to a low-lying ligand field excited state is not likely to be a significant issue at 77 K. The lifetimes of the MLCT excited states of this group of complexes decrease systematically as the number of N−H moieties coordinated to $Ru^{II}$ increases.[25] High frequency vibrational modes in a molecule are expected to relatively efficiently quench an electronic excited state.[26−29] However, $E_{eg}^{00}$ decreases as the number of NH moieties increases, and the two contributions to lifetimes of the complexes are difficult to separate. Am(m)ine perdeuteration results in increases in emission lifetimes; $k_{NH}/k_{ND}$ increases from less than 2 to more than 3 as the number of NH moieties increases. This contrasts markedly with the effect of am(m)ine perdeuteration on the $^2$E emissions of some $Cr^{III}$ complexes,[30] or on the transition metal-to-transition metal electron-transfer emissions of $Cr^{III}(CN^-)Ru^{II}$ complexes.[31] For these complexes, the ratio of lifetimes, $\tau_D/\tau_H$, is roughly proportional to the number (or degeneracy) of coordinated N−H moieties. However, the ratios of lifetimes may not be a definitive indicator of the contribution of high-frequency modes since the heavy isotope (C−D or N−D) may also have a significant role in quenching the excited state. If this were to be the case, then the degeneracy factors would approximately cancel in the ratio of lifetimes.

The work reported here has utilized of the transferability of the basic parameters derived from thermal measurements on electron-transfer systems to guide the search for optical emissions. Several important, but difficult, issues (exchange energies, frozen solvent modes, etc.) have been deferred to a later report. The general theoretical basis for the interrelationships between the different measurements under ambient conditions is well-known,[17,32−35] and applications of the basic arguments to the MLCT absorptions and emissions of polypyridyl complexes have been reported.[9−12,16,36] However, the usefulness of the simplest level of these relationships has not been widely appreciated, as is evidenced in the general acceptance of the claim that $[Ru(NH_3)_4(bpy)]^{2+}$ does not emit. Some of this reluctance to apply electron-transfer concepts to MLCT excited states of polypyridyl complexes may arise from the expectation that the simple arguments will “break down” when the donor−acceptor coupling (manifested in the very large absorptivities) is as strong as it is in these complexes. However, the deviations from the simple diabatic (or zero coupling) limit are a function of the extent of electron delocalization. Since the vertical energy differences are relatively large in these complexes, the extent of electron delocalization is small, and the deviations from the diabatic limit can be treated with standard perturbation theory.[9−13,19]

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(23) Matyushov, D. V.; Newton, M. D. *J. Phys. Chem. A* **2001**, *105*, 8516.

(24) Matyushov, D. V.; Voth, G. A. *J. Phys. Chem. A* **2000**, *104*, 6470.

(25) The lifetime, as well as the emission spectrum reported for $[Ru(en)_2(bpy)]^{2+}$ in ref 1, appears to be that of $[Ru(en)(bpy)_2]^{2+}$.

(26) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

(27) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

(28) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.

(29) Kenkre, V. M.; Tokmakoff, A.; Fayer, M. D. *J. Chem. Phys.* **1994**, *101*, 10618.

(30) Ryu, C. K.; Lessard, R. B.; Lynch, D.; Endicott, J. F. *J. Phys. Chem.* **1989**, *93*, 1752.

(31) Endicott, J. F.; McNamara, P. G.; Buranda, T.; Macatangay, A. V. *Coord. Chem. Rev.* **2000**, *208*, 61.

(32) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1967.

(33) Hush, N. S. *Prog. Inorg. Chem.* **1968**, *8*, 391.

(34) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(35) Hush, N. S. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, D.C., 1982; p 301.

(36) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.